Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 393–396

New sparse polymethylsiloxane dendrimers

**Elena Yu. Katarzhnova, Elena A. Tatarinova, Galina M. Ignat'eva,
Nataliya G. Vasilenko, Ivan B. Meshkov and Aziz M. Muzafarov**

Materials and Equipment

The following reagents and supporting compounds were used in this work: triethoxymethylsilane, diethoxydimethylsilane, trichloromethylsilane, dichloromethylphenylsilane from Acros Organic; $SOCl_2$ and NaOH from LLC Ruskhim.ru; hexane 97.76% from LLC Ruskhim.ru; toluene of analytical grade from LLC Khimpromtorg; and tetrahydrofuran (THF) 99.8% from LLC Ruskhim.ru.

GPC analysis was performed on a Shimadzu LC-10A chromatograph (Japan) with an RID-10A refractometer and an SPD-M10A detector with a diode array, 7.8x300 mm columns, Phenogel sorbent (Phenomenex USA), pore size 500 Å, toluene + 2% THF as the eluent, flow rate 1 ml min^{-1}, temperature 40°C.

Dendrimer samples were purified with a Shimadzu preparative chromatographic system (Japan, Germany): Shimadzu LC-20AT high-pressure pump; RID-20A detector-refractometer; Shimadzu SIL-10ADvp automatic injector; Shimadzu FRC-10A automatic fraction collector; 300×21.2 mm column, Phenogel (Phenomenex, USA), pore size 500A; toluene as the eluent; flow rate 5 ml min^{-1}.

^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer in $CDCl_3$ solutions. ^{29}Si NMR spectra were recorded on a Bruker Avance AV-300 spectrometer (300 MHz) with TMS as the internal standard and $CDCl_3$ as the solvent. Thermal analysis of dendrimers was performed using a DSC-3 differential scanning calorimeter (Mettler-Toledo, Switzerland) with a heating rate of 10 K/min.

GLC analysis was performed on a "Chromatek Analytic 5000" chromatograph (Russia) using a catharometer detector, helium as the carrier gas, 2 m x 3 mm columns, and SE-30 (5%) stationary phase applied on Chromaton-H-AW. Recording and processing of data was carried out using the "Chromatek Analytic" program (Russia).

Experimental

$Me_2(EtO)Si\text{-}ONa$ and $Me(EtO)_2Si\text{-}ONa$ were obtained by the technique reported previously [E. A. Rebrov, A. M. Muzafarov, *Heteroatom Chemistry*, 2006, **17**, 514]. Trimethylsilanol $Me_3Si\text{-}OH$ was obtained as reported [R. R. Khairova, S. A. Milenin, G. V. Cherkaev, I. I. Stoikov, A. M. Muzafarov, *Russ. Chem. Bull., Int. Ed.*, 2016, **65**, 1285].

G0(sp)(OEt), **(1)**, $\{Si_4^3\ (OEt)\}$. Under argon, a solution of $MeSiCl_3$ (56.33 g, 0.377 mol) in dry hexane (200 ml) was added dropwise to $Me_2(OEt)Si\text{-}ONa$ (160.76 g, 1.131 mol) dry hexane (570 ml at -55 °C with intensive stirring. The mixture was allowed to reach room temperature, and stirring was continued for 5 h. The precipitate was separated by filtration. After removing the solvent on a rotary evaporator and fractionating the crude product under reduced pressure (100 mbar), 105.28 g (69.7%) of the fraction with bp 195-8 °C and a purity of ~93% was collected :

^{1}H NMR δ (250MHz $CDCl_3$): 3.75 (q, 6H, J 7.0 Hz, -SiO-C**H**$_2$-CH_3), 1.20 (t, 9H, J 7.0 Hz, -SiO-CH_2-C**H**$_3$), 0.09 (s, 18H, -(C**H**$_3$)SiO_2), 0.13 (s, 3H, -(C**H**$_3$)SiO_3).

G0(sp)(Cl), **(2)**, {Si_4^3(Cl)}. Compound **1** (10.13 g, 0.025 mol) was boiled with $SOCl_2$ (36.07 g, 0.303 mol) $SOCl_2$ in the presence DMF (0.55 g, 0.008 mol) at 90 °C with intensive stirring. After 9 hours, the mixture was cooled down to the room temperature, and the volatiles were removed under reduced pressure. The obtained liquid residue, 9.3 g (98.8%), was dissolved in dry hexane (25 ml). The Cl content in the solution is 8.58%. ^{1}HNMR δ (250MHz $CDCl_3$): 0.48 (s, 18H, -OSi(C**H**$_3$)$_2$Cl), 0.21 (s, 3H, -SiO(C**H**$_3$)$_3$).

G1(sp)(OEt)$_2$, **(6),** {Si_7^6(OEt)}. Under conditions similar to the synthesis of compound **1**, the reaction of Me(EtO)$_2$Si-ONa (7.99 g, 0.046 mol) dissolved in dry toluene (36 ml) and solution of compound **2** (5.72 g) in dry hexane (20 ml, Cl content 0.046 mol) was carried out. The reaction mixture was filtered, and the volatiles were removed under reduced pressure to leave 10.44 g (95.4%) of the crude product of 88% purity. ^{1}H NMR δ (250MHz $CDCl_3$): 3.76 (q, 12H, J 7.0 Hz, -SiO-C**H**$_2$-CH_3), 1.19 (t, 18H, J 7.0 Hz -SiO-CH_2-C**H**$_3$), Σ 0.12 - 0,09 (s, 30H, -(C**H**$_3$)SiO).

G1(sp)(Cl)$_2$, **(7)**, {Si_7^6(Cl)}. Under conditions similar to synthesis **2**, compound **6** (10 g, 0.015 mol) and $SOCl_2$ (40.04 g, 0.337 mol) were reacted in the presence of DMF (0.61 g, 0.008 mol) for 15 h. After removing the volatiles under reduced pressure 8.85 g (90.7%) of the liquid product was obtained. The product was dissolved in dry hexane (50 ml), the Cl content in the solution was 6.38%. ^{1}H NMR δ (250MHz $CDCl_3$): 0.78 (s, 9H, -OSi(C**H**$_3$)Cl_2), 0.21 (s, 21H, -(C**H**$_3$)SiO).

G1(sp)(OEt), **(8)**, {Si_{13}^6(OEt)}. Under conditions similar to the synthesis of compound **6**, the reaction of Me_2(OEt)Si-ONa (9.92 g, 0.070 mol) dissolved in dry toluene (55ml) and the above solution of chloro dendrimer **7** in dry hexane (45 ml, Cl content 0.070 mol) was carried out. The reaction mixture was filtered, and the volatiles were removed under the reduced pressure to leave 11.5 g (86.5%) of the crude liquid product of 77.3% purity. ^{1}H NMR δ (250MHz $CDCl_3$): 3.73 (q, 6H, J 7.0 Hz, -SiO-C**H**$_2$-CH_3), 1.19 (t, 9H, J 7.0 Hz, -SiO-CH_2-C**H**$_3$), 0.10 (s, 66H, -(C**H**$_3$)SiO).

G1(sp)(Cl), **(9),** {Si_{13}^6(Cl)}. Under conditions similar to the synthesis compound **2**, reactant **8** **(**11.5 g, 0.010 mol) and $SOCl_2$ (28.36 g, 0.238 mol) were reacted in the presence of DMF (0.44 g, 0.006 mol) for 12 h. After removing the volatiles under reduced pressure, 10.4 g (95.1%) of the liquid product was obtained which was dissolved in dry hexane (50 ml). The Cl content in the solution is 4.87%. ^{1}HNMR δ (250MHz $CDCl_3$): 0.46 (s, 36H, -O-Si(C**H**$_3$)$_2$Cl), 0.13 (s, 30H, -(C**H**$_3$)SiO_3).

Synthesis of **G-0(sp)(OSiMe$_3$) (5) .** A solution of compound **2** (11.78 g) in dry hexane (Cl content = 0.041 mol) was added dropwise at -40°C in an argon flow to trimethylsilanol (11.00 g, 0.122 mol) and pyridine (3.52 g, 0.045 mol) at the rate that the temperature did not exceed -25°C. The suspension was stirred for 5 h at room temperature until pH value became neutral. The solution was washed with water, dried with Na_2SO_4, and the solvent was evaporated at 2 mbar to leave 3.83 g (55.3%) of the crude product with a GPC purity of 78.1%. Purification by preparative chromatography yielded 1.81 g of the pure product. $Si_7C_{16}H_{48}O_6$, mol. mass (calc.) 533.15 g/mol. ^{1}H NMR δ (250MHz $CDCl_3$): 0.08 (s, 27H, - SiO (C**H**$_3$)$_3$), 0.05 (s, 21H, -(C**H**$_3$)SiO). ^{29}Si NMR δ (60MHz $CDCl_3$): 7.53 (s, O**Si**(CH_3)$_3$), -21.37 (s, -(CH_3)$_2$**Si**O$_2$), -67.33 (s, -(CH_3) **Si**O$_3$).

Synthesis of **G-1(sp)(OSiMe$_3$) (4).** The reaction of trimethylsilanol (7.76 g, 0.086 mol), pyridine (2.50 g, 0.032 mol) and a solution of compounds **9** (28.81 g) in hexane (Cl content = 0.029 mol) was carried out under conditions similar to the synthesis of compound **5**. The mixture was stirred for 7 h and cooled down to room temperature. After the process completion, the medium was neutral. The mixture was treated and the product was isolated similarly to the synthesis of compound **5**. The crude product (4.57 g, 67.2%) had a GPC purity of 56.0%. Purification by preparative chromatography yielded 1.82 g of the pure product. $Si_{19}C_{40}H_{120}O_{18}$, mol. mass (calc.) 1423.00 g/mol. ^{1}H NMR δ (250MHz $CDCl_3$): 0.04 - 0.08 (s, 120H, -(C**H**$_3$)SiO). ^{29}Si NMR δ (60MHz $CDCl_3$): 7.23 (s, O**Si**$(CH_3)_3$); -21.64 (s, -$(CH_3)_2$**Si**O_2); -67.43 (s, -(CH_3) **Si**O_3).

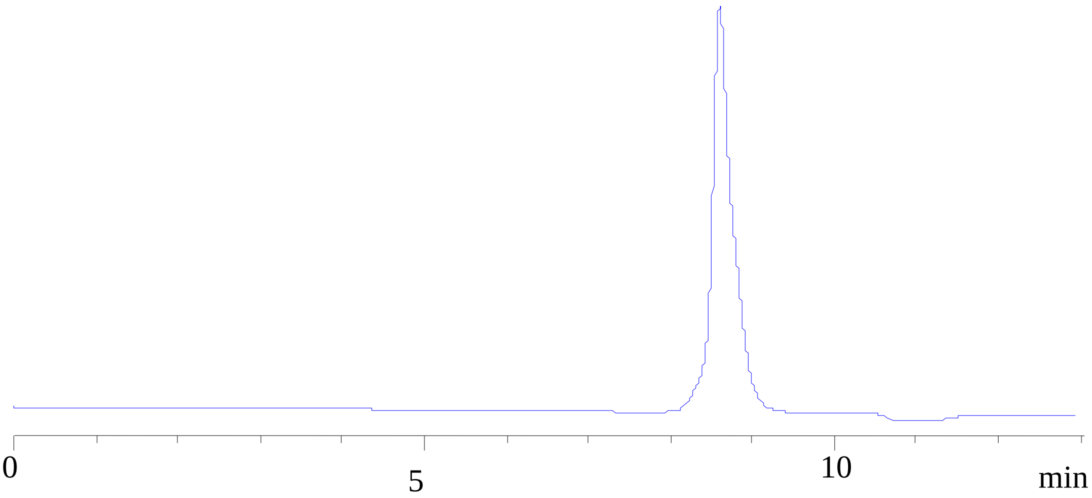

Figure S1 GPC curve of dendrimer **5** after purification.

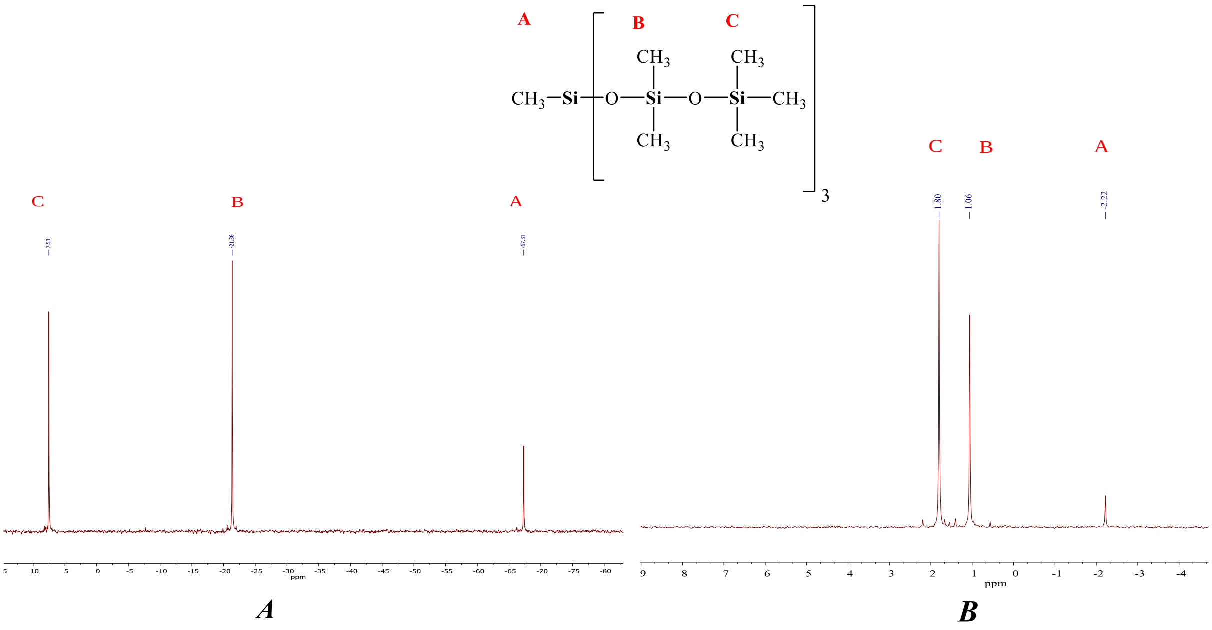

Figure S2 NMR spectra of dendrimer **5**: (A) ^{29}Si NMR, (B) ^{13}C NMR.

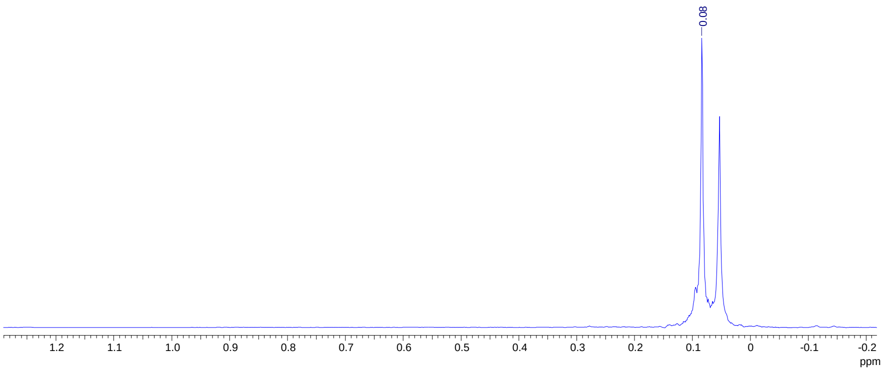

Figure S3 ^{1}H NMR spectrum of **G0(sp)(OSiMe$_3$), (5)** dendrimer.

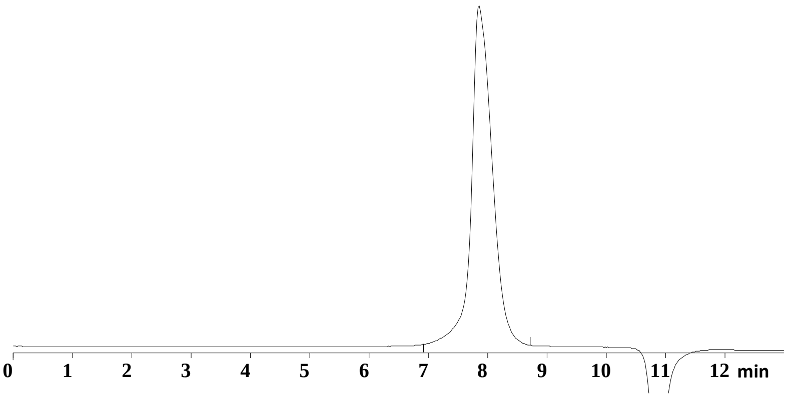

Figure S4 GPC curve of purified **G-1(sp)(OSiMe$_3$), (4)** dendrimer.

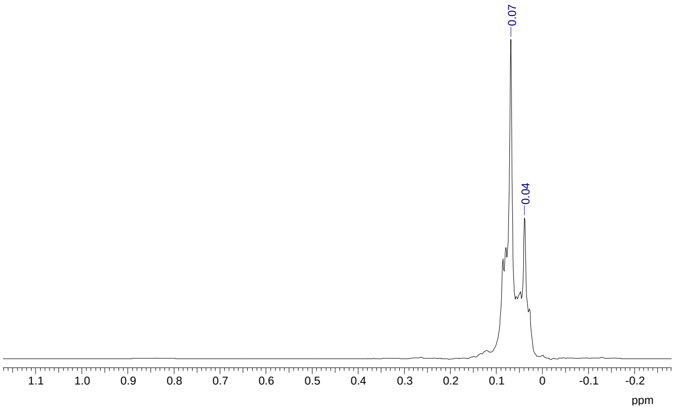

Figure S5 ^{1}H NMR spectrum of **G-1(sp)(OSiMe$_3$), (4)** dendrimer.

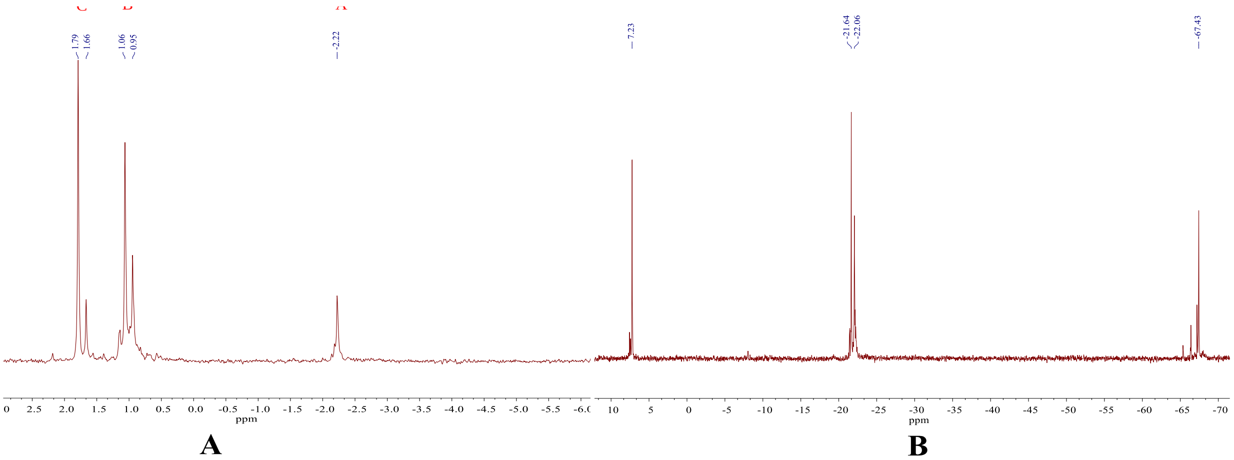

Figure S6 NMR spectra of dendrimer **4**: (A)- ^{13}C NMR, (B)- ^{29}Si NMR.

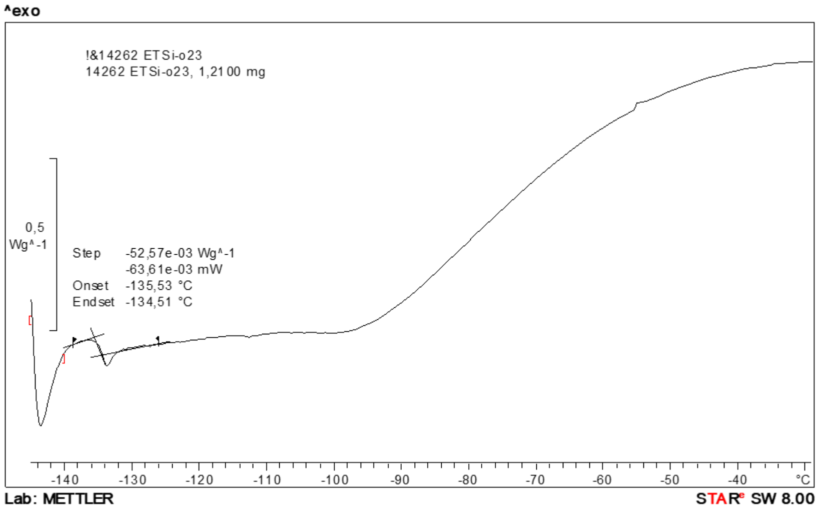

Figure S7 DSC curve of dendrimer **5**.